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medullares. The upper olivary bodies (which were first pointed out by the author in 1857, and subsequently described by Schroeder van der Kolk) and the trapezium are further investigated in a comparison between those of man, the orang outang, and different orders of mammals. The structure of the entire medulla oblongata in the monkey is likewise compared with that of man. The paper concludes with the physiological and pathological application of its contents.

II. "On Pyrophosphoric Acid with the Pyro- and Tetra-phosphoric Amides." By J. H. Gladstone, Ph.D., F.R.S. Received May 9, 1867.

From time to time I have communicated to the Chemical Society descriptions of certain bodies which are best viewed as amides of pyrophosphoric acid; and in pursuing the inquiry I have recently obtained some fresh results, and a new class of compounds. I propose continuing to send the details to the Chemical Society, but I may be permitted to submit to the Royal Society a condensed account of the main facts arrived at in the whole investigation, and a theory of the formation of these substances.

Pyrophosphoric acid is, in the notation now generally adopted, $P_2 H_4 O_7$. In an examination of its ferric compounds, I found evidence of the existence, in solution, of the double salt $P_2 Na_2 fe_2 O_7$*. A more remarkable fact is that the complete ferric salt, and several other pyrophosphates, can exist in an allotropic condition. Thus pure $P_2 fe_4 O_7$, prepared by double decomposition, dissolves readily in dilute sulphuric acid; but on heating the solution it separates in a form which is almost insoluble in the acid. When these allotropic salts are decomposed, the acid produced appears to have the ordinary properties. It is a *pyrophosphate* which is formed, when oxychloride of phosphorus is attacked by a strong aqueous solution of an alkali.

Pyrophosphoric acid exhibits a great tendency to form acid amides. It is only necessary to neutralize it with ammonia to get a body which, when treated with a metallic salt not in excess, gives more or less of a *pyrophosphamate* of the metal, thus:—

$$P_2 H_4 O_7 + 4NH_3 + 3fe\,Cl = P_2 (NH_2) fe_3 O_6 + H_2 O + 3NH_4 Cl.$$

Pyrophosphamic acid, $P_2 (NH_2) H_3 O_6$, may be also prepared by breaking down the higher amides. It is similar in most of its properties to pyrophosphoric acid, but is tribasic. Its ferric salt has also an allotropic modification; when heated with an acid it becomes far less soluble in sulphuric acid, ferric chloride, or pyrophosphate of sodium.

Pyrophospho-diamic acid, $P_2 (NH_2)_2 H_2 O_5$, is produced in a variety of ways, of which the most noteworthy are the action of ammonia on phosphoric anhydride, of ammonia and water on oxychloride of phosphorus, of alcohol or soluble bases on chlorophosphuret of nitrogen, as well as the breaking down of amides of more complicated structure. It is bibasic, and forms salts which are generally very soluble, like itself, in water and alcohol.

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* In order to avoid great complexity of formulæ, Williamson's *Ferricum*, fe=18·66, has been adopted.

Pyrophospho-triamic acid, $P_2\,(NH_2)_3\,HO_4$, is formed when oxychloride of phosphorus is saturated with ammonia at about 100° C., and the resulting mass is treated with water, or when tetraphospho-pentazotic acid is exposed to the action of water for some time. It is nearly insoluble in water, and so are its combinations, even those with the alkaline metals. It readily decomposes most soluble salts, giving rise to compounds in which 1, 2, 3, or 4 atoms of hydrogen are replaced. With slightly acid nitrate of silver it gives a white salt, $P_2\,(NH_2)_3\,Ag\,O_4$; with the ammoniacal nitrate a bright yellow salt, $P_2\,N_3\,H_4\,Ag_3\,O_4$.

By the action of water on the compounds of ammonia with oxychloride of phosphorus, there are also produced some acid amides that belong to a higher series. Great difficulty was experienced in being certain of the purity of any specimen of these compounds; hence some doubt may still rest on their ultimate composition.

Tetraphospho-tetramic acid, $P_4\,(NH_2)_4\,H_2\,O_9$, is a solid stable body, insoluble in alcohol, but soluble in water, and combining readily with bases, the amount of hydrogen replaced appearing to vary from 1 to 6 atoms.

Terammoniated Tetraphospho-diamic acid, $P_4\,(NH_2)_2\,N_3\,H_{13}\,O_{11}$.—This is a viscid liquid, insoluble in alcohol, but very soluble in water. It forms a liquid combination with ammonia; but metallic salts appear to break it up into a variety of compounds. By the action of heat, boiling water, strong acids, or alkaline carbonates, tetraphospho-tetramic acid may be produced from it. Among the bodies formed when it is heated *per se* is a white substance, insoluble, or nearly so, in cold water, having the ultimate composition $PNH_4\,O_3$. This is at once transformed into pyrophospho-diamic acid by hot water, or dilute acids.

Tetraphospho-pentazotic acid, $P_4\,N_5\,H_9\,O_7$, is formed when oxychloride of phosphorus is fully saturated with ammonia, and the resulting mass is heated at about 230° C., and washed with cold water. It is an insoluble body, capable of decomposing metallic salts. One atom of hydrogen is replaceable by potassium or ammonium. When treated with slightly acidulated nitrate of silver, it gives a tetrazotic salt, $P_4\,N_4\,H_4\,Az_2\,O_7$, which, when decomposed by mineral acids, yields tetraphospho-tetramic acid and other compounds.

Amidated Oxychlorides of Phosphorus.—The oxychloride will absorb either 2 or 4 molecules of ammonia; and there can be little doubt that the resulting white solids consist of chloride of ammonium mixed with $P\,(NH_2)\,Cl_2\,O$ in the one case, and $P\,(NH_2)_2\,Cl\,O$ in the other, but I have never succeeded in separating them in a condition fit for analysis.

If either of these compounds be strongly heated, hydrochloric acid, or chloride of ammonium, is given off, and there remains *phosphonitryle*, PNO.

By the action of heat on the substances already described, other compounds may also be prepared, thus:—

Pyrophospho-nitrylic acid.—If pyrophospho-triamate of potassium be heated at a dull redness, it loses two-thirds of its nitrogen as ammonia, leaving a fused mass, which is insoluble in water, but forms compounds when treated with silver or copper salts. These have the composition of pyrophospho-nitrylates, $P_2\,N\,Ag\,O_4$. If pyrophospho-triamic acid itself be similarly heated, it parts with one molecule of ammonia, and gives a body, $P_2\,N_2\,H_4\,O_4$, isomeric with pyrophospho-nitrylate of ammonium, which is speedily resolved by damp air into pyrophosphamic acid and other compounds.

The process adopted for the analysis of these acid amides was that of boiling them with strong hydrochloric acid. This converts them all into ammonia and ordinary phosphoric acid, which were determined in the usual manner.

Theoretical Constitution.

A difficulty in understanding the formation of the bodies above described from oxychloride of phosphorus arises from the fact that they contain P_2... or P_4..., while the original phosphorus compound contains but one atom of that element. The following considerations may furnish a probable explanation and reveal their true constitution.

When a chloride and water act on one another, three different courses are open, each giving hydrochloric acid as one of the results. In the first case the chlorine combines with one of the atoms of hydrogen, while the remaining hydroxyl, HO, takes its place in the original compound, thus:—

$$P\,Cl_3 + 3\,H_2\,O = 3\,H\,Cl + P\,H_3\,O_3 \ (\textit{phosphorous acid}).$$

In the second case two atoms of chlorine simultaneously attack the two atoms of hydrogen, and the liberated single atom of oxygen takes their place, thus:—

$$P\,Cl_5 + H_2\,O = 2\,H\,Cl + P\,Cl_3\,O \ (\textit{oxychloride of phosphorus}).$$

In each of these cases we may consider the new compound as formed on the same type as the original chloride, only the chlorine is differently replaced.

In the one case $P\begin{matrix}Cl\\Cl\\Cl\end{matrix}$ becomes $P\begin{matrix}H\,O\\H\,O,\\H\,O\end{matrix}$

and in the other $P\begin{matrix}Cl\\Cl\\Cl\end{matrix}\begin{matrix}Cl\\Cl\end{matrix}$ becomes $P\begin{matrix}Cl\\Cl\,O.\\Cl\end{matrix}$

But there is a third case in which the two atoms of hydrogen in water are attacked simultaneously by two atoms of the chloride, and the result is that the oxygen is left in combination with two molecules of the substance originally combined with the chlorine. Here it is simplest to consider that it is the water type which is preserved.

It is this third mode of action which explains the production of the compounds containing P_2... and P_4....

If we act on oxychloride of phosphorus with water, a slow replacement of the chlorine takes place, each atom decomposing a molecule of water, and the result is—

$$\begin{matrix}\mathrm{Cl}\\ \mathrm{P\,Cl\,O}\\ \mathrm{Cl}\end{matrix}+3\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}=3\mathrm{H\,Cl}+\begin{matrix}\mathrm{H\,O}\\ \mathrm{P\,H\,O\,O}\\ \mathrm{H\,O}\end{matrix},$$

which is $P\,H_3\,O_4$, *tribasic* or *ortho-phosphoric acid.* If, however, we employ strong solutions of potash or ammonia, the result is totally different. We now obtain salts of an acid formed not on the type of the oxychloride, but on the type of the alkaline hydrate, or water. To explain this the reaction must be broken up into two stages, though it is not improbable that these may occur simultaneously in nature. These stages are—

$$2\mathrm{P\,Cl_3\,O}+\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}=\mathrm{K\,Cl}+\mathrm{H\,Cl}+\left.\begin{matrix}\mathrm{P\,Cl_2\,O}\\ \mathrm{P\,Cl_2\,O}\end{matrix}\right\}\mathrm{O},$$

$$\left.\begin{matrix}\mathrm{P\,Cl_2\,O}\\ \mathrm{P\,Cl_2\,O}\end{matrix}\right\}\mathrm{O}+4\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}=4\mathrm{K\,Cl}+\left.\begin{matrix}\mathrm{P\,(H\,O)_2\,O}\\ \mathrm{P\,(H\,O)_2\,O}\end{matrix}\right\}\mathrm{O},$$

which is $P_2\,H_4\,O_7$, *pyrophosphoric acid.*

There still remains another mode of action, the replacement of 2 Cl in the oxychloride by O, and this may be expressed in the two following stages,

$$\mathrm{P\,Cl_3\,O}+2\left.\begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}=2\mathrm{K\,Cl}+\mathrm{P\,Cl\,O\,O},$$

$$\mathrm{P\,Cl\,O\,O}+\left.\begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}=\mathrm{K\,Cl}+\mathrm{P\,(K\,O)\,O\,O},$$

which is $P\,K\,O_3$, *metaphosphate of potassium.* And this is actually produced when the oxychloride is dropped on oxide of potassium, and a similar reaction takes place with dry sesquicarbonate of ammonium.

Reverting to pyrophosphoric acid, if $\left.\begin{matrix}\mathrm{P\,(H\,O)_2\,O}\\ \mathrm{P\,(H\,O)_2\,O}\end{matrix}\right\}\mathrm{O}$ be its rational formula, it is easy enough to understand that amides are readily formed, and to see how upon neutralizing it with ammonia, one molecule of H O is apt to be replaced by $N\,H_2$, giving $\left.\begin{matrix}\mathrm{P\,(N\,H_2)\,(N\,H_4\,O)\,O}\\ \mathrm{P\,(N\,H_4\,O)_2\,O}\end{matrix}\right\}\mathrm{O}$, the pyrophosphamate, instead of $\left.\begin{matrix}\mathrm{P\,(N\,H_4\,O)_2\,O}\\ \mathrm{P\,(N\,H_4\,O)_2\,O}\end{matrix}\right\}\mathrm{O}$, the pyrophosphate of ammonium.

Nor is it difficult to understand the formation of pyrophosphodiamic acid, when we start not with the oxychloride, but with the amidated oxychloride of phosphorus. The two stages, analogous to those given above for the formation of pyrophosphoric acid, will be

$$2P(NH_2)Cl_2O + \left.\begin{matrix}H\\H\end{matrix}\right\}O = 2HCl + \left.\begin{matrix}P(NH_2)ClO\\P(NH_2)ClO\end{matrix}\right\}O,$$

$$\left.\begin{matrix}P(NH_2)ClO\\P(NH_2)ClO\end{matrix}\right\}O + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O = 2HCl + \left.\begin{matrix}P(NH_2)(HO)O\\P(NH_2)(HO)O\end{matrix}\right\}O,$$

which is $P_2(NH_2)_2H_2O_5$, *pyrophospho-diamic acid.*

The symmetry of this reaction would be lost were pyrophosphamic acid produced, and, indeed, it seems never to occur among the substances actually formed.

But the pyro-diamic acid may be equally produced, if we start with the higher amidated oxychloride formed at a low temperature. In this case it is necessary to suppose that while two molecules of the phosphorus compound attack one molecule of water, two other molecules of water give rise to the usual replacement of HO for NH_2. The two stages are precisely analogous to those given above, but are probably simultaneous, the reaction being favoured by the affinity of the hydrochloric acid for the ammonia,

$$2P(NH_2)_2ClO + \left.\begin{matrix}H\\H\end{matrix}\right\}O = 2HCl + \left.\begin{matrix}P(NH_2)_2O\\P(NH_2)_2O\end{matrix}\right\}O,$$

$$\left.\begin{matrix}P(NH_2)_2O\\P(NH_2)_2O\end{matrix}\right\}O + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O = 2NH_3 + \left.\begin{matrix}P(NH_2)(HO)O\\P(NH_2)(HO)O\end{matrix}\right\}O,$$

which, as before, is $P_2(NH_2)_2H_2O_5$, *pyrophospho-diamic acid.*

The formation of *pyrophospho-triamic acid* is dependent on some alteration in the amidated oxychloride, when produced at a high temperature. As the nature of this change is unknown, it may be better not to speculate on the intermediate stages, but the result of the action on water would seem to be $\left.\begin{matrix}P(NH_2)(HO)O\\P(NH_2)_2O\end{matrix}\right\}O$, or $P_2(NH_2)_3HO_4$.

If this be the true explanation of the manner in which the pyrophosphoric amides are formed, it will equally explain the formation of the tetraphosphoric compounds. It does not follow that when two molecules of the amidated oxychloride have attacked one of water to form $\left.\begin{matrix}P(NH_2)ClO\\P(NH_2)ClO\end{matrix}\right\}O$, that is, $P_2(NH_2)_2Cl_2O_3$, the remaining chlorine should be replaced by HO. The process of attacking both atoms of hydrogen in water may be repeated, thus—

$$2P_2(NH_2)_2Cl_2O_3 + \left.\begin{matrix}H\\H\end{matrix}\right\}O = 2HCl + \left.\begin{matrix}P_2(NH_2)_2ClO_3\\P_2(NH_2)_2ClO_3\end{matrix}\right\}O,$$

which, when acted on by water in the usual way, gives

$$\left.\begin{matrix}P_2(NH_2)_2ClO_3\\P_2(NH_2)_2ClO_3\end{matrix}\right\}O + 2\left.\begin{matrix}H\\H\end{matrix}\right\}O = 2HCl + \left.\begin{matrix}P_2(NH_2)_2(HO)O_3\\P_2(NH_2)_2(HO)O_3\end{matrix}\right\}O,$$

which is $P_4(NH_2)_4H_2O_9$, *tetraphospho-tetramic acid.* And this compound, like the pyro-diamic acid, may be prepared from the higher amidated oxychloride, and the process is capable of the same explanation. The three stages, probably simultaneous, are as follows:—

$$2\mathrm{P(NH_2)_2ClO}+\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}=2\mathrm{HCl}+\left.\begin{matrix}\mathrm{P(NH_2)_2O}\\ \mathrm{P(NH_2)_2O}\end{matrix}\right\}\mathrm{O}\text{ or }\mathrm{P_2(NH_2)_4O_3},$$

$$2\mathrm{P_2(NH_2)_4O_3}+\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}=2\mathrm{NH_3}+\left.\begin{matrix}\mathrm{P_2(NH_2)_3O_3}\\ \mathrm{P_2(NH_2)_3O_3}\end{matrix}\right\}\mathrm{O},$$

$$\left.\begin{matrix}\mathrm{P_2(NH_2)_3O_3}\\ \mathrm{P_2(NH_2)_3O_3}\end{matrix}\right\}\mathrm{O}+2\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}=2\mathrm{NH_3}+\left.\begin{matrix}\mathrm{P_2(NH_2)_2(HO)O_3}\\ \mathrm{P_2(NH_2)_2(HO)O_3}\end{matrix}\right\}\mathrm{O},$$

which is $\mathrm{P_4(NH_2)_4H_2O_9}$, *tetraphospho-tetramic acid.*

The *tetraphosphoric acid*, of which this is the fourth amide, must be $\mathrm{P_4H_6O_{13}}$, a substance already known, at least in its salts, for it is Fleitmann and Henneberg's phosphoric acid.

On the view given above the rational formulæ of the four phosphoric acids may be thus expressed:—

Ortho-phosphoric acid.........	$\mathrm{P(HO)_3O}.$
Meta-phosphoric acid	$\mathrm{P}\left\{\begin{matrix}\mathrm{HO}\\ \mathrm{O}\end{matrix}\right\}\mathrm{O}.$
Pyro-phosphoric acid	$\left.\begin{matrix}\mathrm{P(HO)_2O}\\ \mathrm{P(HO)_2O}\end{matrix}\right\}\mathrm{O}.$
Tetra-phosphoric acid	$\left.\begin{matrix}\left.\begin{matrix}\mathrm{P(HO)_2O}\\ \mathrm{P(HO)\;O}\end{matrix}\right\}\mathrm{O}\\ \left.\begin{matrix}\mathrm{P(HO)_2O}\\ \mathrm{P(HO)\;O}\end{matrix}\right\}\mathrm{O}\end{matrix}\right\}\mathrm{O}.$

It is more difficult to assign satisfactory rational formulæ to the two compounds containing $\mathrm{P_4N_5}$.... The fact that the atoms of nitrogen are uneven in number destroys the symmetry, and seems to point to their being products of decomposition of substances containing $\mathrm{P_4N_6}$.... That they both belong to the tetraphosphoric series is evidenced by their giving rise easily to tetraphospho-tetramic acid.

The reactions of the liquid $\mathrm{P_4N_5H_{17}O_{11}}$ indicate that it is an acid ammonium salt, or is readily transformable into such. Hence I have called it *terammoniated tetraphospho-diamic acid*, and its formula will be

$$\left.\begin{matrix}\left.\begin{matrix}\mathrm{P(NH_2)(NH_4O)O}\\ \mathrm{P\qquad\;(NH_4O)O}\end{matrix}\right\}\mathrm{O}\\ \left.\begin{matrix}\mathrm{P(NH_2)(HO)\quad O}\\ \mathrm{P\qquad\;(NH_4O)O}\end{matrix}\right\}\mathrm{O}\end{matrix}\right\}\mathrm{O},\text{ or }\mathrm{P_4(NH_2)_2(NH_4)_3HO_{11}}.$$

The formation of a tetraphospho-tetramate from a salt of this structure would be analogous to the ready passage of pyrophosphate of ammonium into a pyrophosphamate.

The acid $\mathrm{P_4N_5H_9O_7}$, to which has been given the provisional name *tetraphospho-pentazotic acid*, is perhaps derived from the decomposition of tetraphospho-hexamide, $\mathrm{P_4(NH_2)_6O_7}$, which is the complete amide of tetraphosphoric acid, and is a very likely substance to be formed by the action of water on $P(NH_2)_2ClO$ that had been exposed to heat, and probably converted into $P_2(NH_2)_4Cl_2O_2$. If this hexamide really exist, it is at once broken down by the freed hydrochloric acid, or by hydrate of potassium, thus—

$$P_4(NH_2)_6O_7+HCl=NH_4Cl+P_4N_5H_9O_7,$$

giving rise naturally to a monobasic acid.

If we regard the compound resulting from the action of nitrate of silver on this acid as containing imidogen NH, instead of amidogen NH_2, it gives a formula of great symmetry of structure—

$$\left.\begin{array}{l}\left.\begin{array}{l}P(NH)AgO\\ P(NH)\quad\;\; O\end{array}\right\}O\\ \left.\begin{array}{l}P(NH)AgO\\ P(NH)\quad\;\; O\end{array}\right\}O\end{array}\right\}O, \text{ or } P_4(NH)_4Ag_2O_7,$$

and the salt would bear the name of *tetraphospho-tetrimate of silver.*

III. "*Ovibos moschatus* (Blainville)." By W. Boyd Dawkins, M.A., F.G.S. Communicated by Prof. Huxley. Received May 9, 1867.

(Abstract.)

Ovibos moschatus, more commonly known as the musk-ox, has been described under different names by naturalists as their opinions fluctuated concerning its affinities with the ox, buffalo, or sheep. It is called the musk-ox by all the arctic explorers, *Bos moschatus* by Schreber, Zimmermann, Pennant, and Cuvier, musk-buffalo allied to the *Bubalus Caffir* of South Africa by Professor Owen, *Ovibos moschatus* by De Blainville, Desmarest, Richardson, and M. Lartet. That the latter four naturalists are right in the place they assign to it in the zoological scale, intermediate between *Ovis* and *Bos*, is proved both by the natural history and the osteology of the animal. The absence of a muffle and dewlap, the hairiness of the nostrils, the shortness of tail and smallness of ear, and the possession of two teats only, separate the animal from *Bos* and connect it with *Ovis*, while the large size and long gestation of nine months differentiate it from the latter animal. Precisely the same evidence is afforded by its skeleton. In the skull, the tapering of the anterior portion, the prominence of the orbit, the verticality of the facial plate of the maxillary, the presence of a larmier, the squareness of the basisphenoid, the presence of the occipito-parietal suture on the coronal surface; in the dentition, the sharpness of the costæ 1,2, and 3, and the absence of the accessory column from the inner interspace of the lobes of the upper teeth are among the chief ovine characters, and throughout the skeleton the same ovine tendency is manifested. With the exception of the great development of horns, there is no point in